η_0 = asymptotic effectiveness factor for $\tau \to 0$
η_∞ = asymptotic effectiveness factor for $\tau \to \infty$
τ_1 = $l(k'S/D_f')^{1/2}$ = Thiele modulus for first-order reaction
τ_1^* = $V_p(k'S/D_f')^{1/2}/A_p$ = modified Thiele modulus for first-order reaction
τ_n = $l[(n+1)C_s^{n-1}k'S/2D_f']^{1/2}$ = Thiele modulus for n^{th}-order reaction
ω = αx_s

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Rectilinear Equation for Binary Azeotropes

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Since Cailletet and Mathias (1886) developed an empirical linear equation to correlate the saturated liquid and vapor densities at the coexistence phases, the so-called Rectilinear Diameter Equation (RDE) has become a convenient way to determine the density at the critical point. The accuracy of the critical density determined by means of RDE has been seriously questioned owing to the relatively poor precision of the measured saturated densities close to the critical state. It is highly important that a theoretical basis for the RDE be established, for then the critical density can be accurately determined from the saturated densities remote from the critical state.

Recently, Zollweg and Mulholland (1972) developed a theoretical model for correlating the saturated densities of the coexisting phases. They have found that within the experimental accuracy the correlated values from the equation derived from the theoretical model of the decorated lattice gas are similar to those from the empirical RDE. It is not the purpose here to strengthen the theoretical foundation for RDE but rather to enlarge its usefulness. The RDE has been applied to correlating the saturated transport properties [Needham and Ziebland (1965) in their correlation of the saturated liquid and vapor thermal conductivities of ammonia in the coexistence phases; Starling, Eakin, Dolan, and Ellington (1962), the rectilinear behavior for the saturated liquid and vapor viscosities of ethane, propane, and *n*-butane in the critical region].

Most recently, Hall and Eubank (1976) have further demonstrated the use of the RDE in correlating the isochoric slopes from the coexistence curve. These are all limited to the pure components.

Won and Prausnitz (1974) observed that the saturated liquid and vapor densities for some binary mixtures obey analogously the rectilinearity rule such that at constant temperature the arithmetic mean of the molar densities of the saturated vapor and the equilibrium saturated liquid is a linear function of pressure.

This note will show that the rectilinear diameter constant of binary azeotropes can be calculated from the constants of the components, and, furthermore, the saturated vapor densities of the azeotrope can be calculated from the corresponding experimental liquid densities.

The reduced RDE for the i^{th} component can be expressed as (Partington, 1949)

$$\tfrac{1}{2}\left(\frac{\rho_{li}+\rho_{vi}}{\rho_{ci}}\right) = 1 + \epsilon_i\left(\frac{T_{ci}-T}{T_{ci}}\right) \qquad (1)$$

When

$$\tfrac{1}{2}\left(\frac{\rho_{li}+\rho_{vi}}{\rho_{ci}}\right) - 1 \text{ -vs.-} \left(\frac{T_{ci}-T}{T_{ci}}\right)$$

is plotted, the rectilinear constant ϵ_i is the linear slope

TABLE 1. RECTILINEAR CONSTANT OF AZEOTROPES

Composition, mole %		Rectilinear constant, ϵ, experimental,	calculated [Equation (2)],	%D
CCl_2F_2/CHF_2CH_3[1]		0.9396	0.9405	0.10
CCl_2F_2	60.4	0.8760		
CHF_2CH_3	39.6	1.0390		
$CHClF_2/CClF_2CF_3$[2]		0.9094	0.90943	0.00
$CHClF_2$	63.0	0.9091		
$CClF_2CF_3$	37.0	0.9100		
CH_2ClF/CCl_2F_2[3]		0.9209	0.9139	0.77
CH_2ClF	19.4	1.0714		
CCl_2F_2	80.6	0.8760		
$SF_6/CHClF_2$[3]		0.9500	0.9358	1.50
SF_6	50.0	0.9625		
$CHClF_2$	50.0	0.9091		
$CHClFCF_3/\overline{CF_2CF_2CF_2CF_2}$[4]		1.0233	1.0237	0.04
$CHClFCF_3$	60.0	1.0118		
$\overline{CF_2CF_2CF_2CF_2}$	40.0	1.0417		

(1) "Properties of Commonly Used Refrigerants," Air Conditioning and Refrigeration Institute, Washington, D.C. (1957).
(2) *ASHRAE Handbook of Fundamentals*, ASHRAE, Chapt. 31, New York (1972).
(3) "Unpublished Data," Allied Chemical Corporation, Buffalo, New York.
(4) Perelstein, I. I., "The Thermodynamic Properties of the Azeotropic Mixture R-124 and RC-318," *Kholodil'naya Tekhnika*, No. 2, 76 (1962).

Table 2. Saturated Vapor Densities CCl_2F_2/CHF_2CH_3 Azeotrope

Temperature, °C	Pressure, atm	Saturated vapor density, g/cm³ Experimental*	Calculated	% dev.
−40.0	0.737	0.3931	0.3915	0.41
−28.9	1.214	0.6252	0.6201	0.84
−17.8	1.902	0.9524	0.9455	0.72
−6.7	2.859	1.4001	1.3993	0.06
4.4	4.146	1.9979	1.9963	0.08
15.6	5.827	2.7830	2.7705	0.45
26.7	7.973	3.8019	3.7838	0.48
37.8	10.654	5.1173	5.1035	0.27
48.9	13.945	6.8182	6.8057	0.18
60.0	17.927	9.0546	9.0375	0.19
71.1	22.680	12.1371	12.1171	0.17

* Properties of "Commonly Used Refrigerants," Air Conditioning and Refrigeration Institute, Washington 6, D.C. (1957).

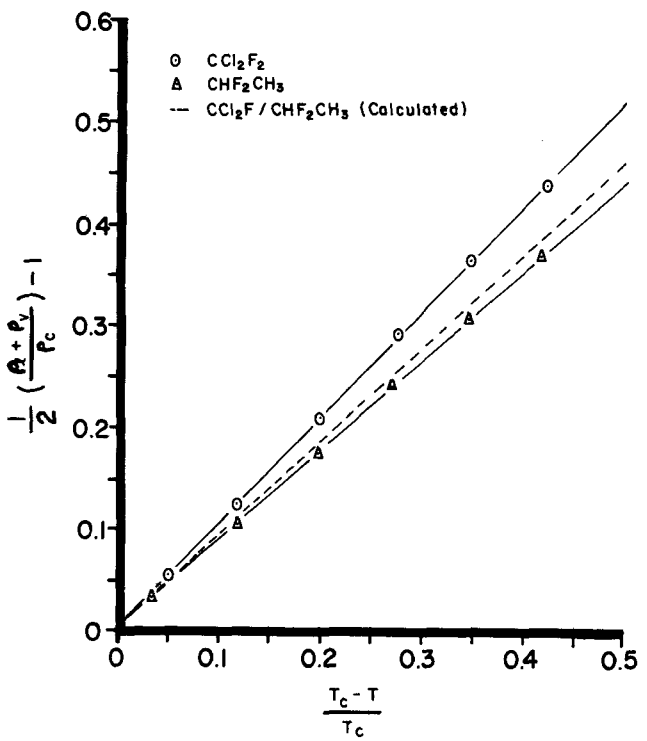

Fig. 1. Rectilinear diameter of CCl_2F_2/CHF_2CH_3 azeotrope.

through the origin.

Intuitively, if it is assumed that the rectilinear constant of the azeotrope is the molar average of the rectilinear constant of the components, then

$$\epsilon_a = \sum_i^n \chi_i \epsilon_i \qquad (2)$$

The calculated rectilinear constants for the fluorocarbon azeotrope from Equation (2) and the constant slope determined from the experimental data of the azeotrope from Equation (1) are shown in Table 1. It can be seen that an excellent agreement is obtained. Consequently, if the critical temperature (Li, 1972), critical density (Chen and Li, 1965), and saturated liquid densities of the azeotrope are accurately known, then the saturated vapor densities can also be accurately calculated. As an illustration, the calculated saturated vapor densities of the azeotropic mixture of (CCl_2F_2/CHF_2CH_3) and its experimental data are shown in Table 2, and the reduced RDE for the azeotrope CCl_2F_2/CHF_2CH_3 and its components are also shown in Figure 1.

The rectilinear behavior observed for the various saturated properties in the coexistence phases leads one to believe that the RDE can be applied to other saturated properties (transport and thermodynamic) for pure compounds and mixtures.

NOTATIONS

ϵ = rectilinear constant
n = number of components
T = absolute temperature, °K
χ = mole fraction
ρ = density, g/cm³

Subscripts

a = azeotrope
c = critical
i = i^{th} component
l = liquid
v = vapor

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